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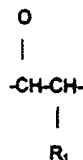
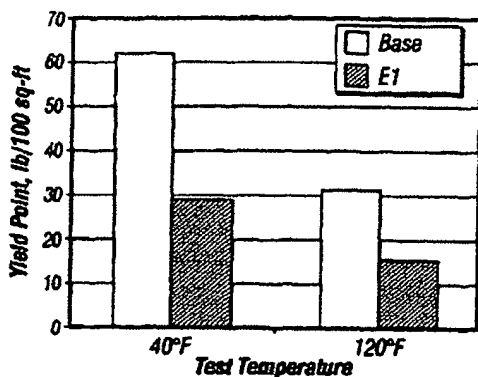
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(54) Title: THINNERS FOR INVERT EMULSIONS



(I)



(II)

(57) Abstract: A method of reducing the viscosity of invert emulsions and oil-based drilling fluids and well service fluids comprising such emulsions over a broad temperature range is disclosed. The method comprises adding to said invert emulsions of the invention a non-ionic surfactant alone or in combination with a co-thinner having the formula: $R^{**}-(C_2H_4O)_n(C_3H_6O)_m(C_4H_8O)_k-H$ where R^{**} is a saturated or unsaturated, linear or branched, alkyl radical having about 8 to about 24 carbon atoms, n is a number ranging from about 1 to about 10, m is a number ranging from about 0 to about 10, and k is a number ranging from about 0 to about 10. The non-ionic surfactant is a reaction product of ethylene oxide, propylene oxide and/or butylene oxide with C_{10-22} carboxylic acids or C_{10-22} carboxylic acid derivatives containing at least in position 9/10 and/or 13/14 structural units of general formula (I) where R_1 is a hydrogen atom or an OH group or a group OR_2 . R_2 is an alkyl group of about 1 to about 18 carbon atoms, an alkenyl group of about 2 to about 18 carbons atoms, or a group of the formula (II): R_3 is a hydrogen atom, an alkyl group of about 1 to about 21 carbon atoms or an alkylene group of 2 to 21

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carbon atoms.

THINNERS FOR INVERT EMULSIONS

Background of the Invention

1. Field of the Invention

5 This invention is generally related to methods and compositions for drilling and servicing wellbores in hydrocarbon bearing subterranean formations. Particularly, this invention is related to oil-based drilling fluid systems comprising water-in-oil invert emulsions, and to thinners that enhance or enable use of such fluids over a broad temperature range.

10 2. Description of Relevant Art

A drilling fluid, or "mud" which a drilling fluid is also often called, is a specially designed fluid that is circulated in a wellbore as the wellbore is being drilled to facilitate the drilling operation. The various functions of a drilling fluid include removing drill cuttings from the wellbore, cooling and lubricating the drill
15 bit, aiding in support of the drill pipe and drill bit, and providing a hydrostatic head to maintain the integrity of the wellbore walls and prevent well blowouts. Specific drilling fluid systems are selected to optimize a drilling operation in accordance with the characteristics of a particular geological formation.

A drilling fluid typically comprises water and/or oil or synthetic oil or other
20 synthetic material or synthetic fluid ("synthetic") as a base fluid, with solids in suspension. A non-aqueous based drilling fluid typically contains oil or synthetic as a continuous phase and may also contain water dispersed in the continuous phase by emulsification so that there is no distinct layer of water in the fluid. Such dispersed water in oil is generally referred to as an invert
25 emulsion or water-in-oil emulsion.

A number of additives may be included in such oil based drilling fluids and invert emulsions to enhance certain properties of the fluid. Such additives may include, for example, emulsifiers, weighting agents, fluid-loss additives or fluid-loss control agents, viscosifiers or viscosity control agents, and alkali.
30 Further general discussion and description of oil-based drilling fluids is provided in P.A. Boyd, et al., New Base Oil Used In Low Toxicity Oil Muds, Journal of

Petroleum Technology, pages 137-142 (1985), which is incorporated herein by reference.

5 An essential criterion for assessing the utility of a fluid as a drilling fluid or as a well service fluid is the fluid's rheological parameters, particularly under drilling and wellbore conditions. For use as a drilling fluid, or as a fluid for servicing a well, the fluid must be capable of maintaining certain viscosities suitable for drilling and circulation in the wellbore. Preferably, a drilling fluid will be sufficiently viscous to be capable of supporting and carrying to the surface of the well drill cuttings without being so viscous as to interfere with the drilling operation. Moreover, a drilling fluid must be sufficiently viscous to be able to suspend barite and other weighting agents. However, increased viscosity can result in problematic sticking of the drill string, and increased circulating pressures can contribute to lost circulation problems.

15 Thinner may be added to the drilling fluid or drilling mud systems before and in the course of drilling. Anionic surfactants particularly from the group of the fatty alcohol sulfates, the fatty alcohol ether sulfates and the alkylbenzenesulfonates are examples of such thinners known in the prior art. Although such compounds have been shown to effect thinning of drilling fluids, their effectiveness as thinners is not always uniform over the entire range of temperatures (typically as low as about 40°F (or lower) to as high as about 250°F (or higher)) at which drilling fluids are used.

20 Thinner and other additives to drilling fluids, as well as drilling fluids employed in onshore and offshore wells, must commonly meet stringent environmental regulations related to biodegradability and toxicity. Further, drilling fluids and additives to drilling fluids must be able to withstand subterranean conditions that the fluids will typically encounter in a wellbore, such as high temperatures, high pressures, and pH changes.

30 A need exists for improved rheology-modifying or viscosity reducing additives to oil-based drilling fluids, and particularly to drilling fluids comprising invert (water-in-oil) emulsions, which are capable of being used over a broad range of temperatures. As used herein, unless indicated otherwise, a "broad

temperature range" shall be understood to generally mean temperatures ranging from about 14°F to about 350°F and preferably ranging from about 40°F to about 250°F.

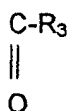
5 Summary of the Invention

According to the method of the present invention, at least one compound or composition is added to a water-in-oil or invert emulsion, or a drilling fluid or well service fluid comprising such emulsion, which reduces the viscosity of the emulsion over a broad temperature range or which enables or enhances the ability of the emulsion to maintain its viscosity over a broad temperature range. The compound or composition, which may be generally called a "thinner," continues to have this effect in a drilling fluid or well service fluid comprising the emulsion for use in drilling or servicing wellbores in subterranean formations, particularly hydrocarbon bearing subterranean formations, over a broad temperature range.

The first such thinner compound of the present invention is a non-ionic surfactant which is a reaction product of ethylene oxide, propylene oxide and/or butylene oxide with C₁₀₋₂₂ carboxylic acids or C₁₀₋₂₂ carboxylic acid derivatives containing at least one double bond in position 9/10 and/or 13/14 having units of the general formula:



where R₁ is a hydrogen atom or an OH group or a group OR₂, where R₂ is an alkyl group of about 1 to about 18 carbon atoms, or an alkenyl group of about 2 to about 18 carbon atoms or a group of the formula:



- 5 where R_3 is a hydrogen atom, or an alkyl group of about 1 to about 21 carbon atoms or an alkylene group of about 2 to about 21 carbon atoms.

This first thinner compound may be used alone or may be used in combination with a second or other thinner or "co-thinner" compound having the following formula:

10



- where R is a saturated or unsaturated, linear or branched, alkyl radical having about 8 to about 24 carbon atoms, n is a number ranging from about 1 to about 10, m is a number ranging from about 0 to about 10, and k is a number ranging from about 0 to about 10.

The invention also comprises an invert emulsion drilling fluid or well service fluid containing this first thinner compound, or containing said first thinner compound in combination with said second thinner compound.

20

Brief Description of the Drawings

Figure 1 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 2.

- Figure 2 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 3.

Figure 3 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 4.

Figure 4 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 5.

- Figure 5 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 6.

Figure 6 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 7.

Figure 7 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 8.

5 Figure 8 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 9.

Figure 9 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 10.

10 Figure 10 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 11.

Figure 11 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 12.

Figure 12 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 13.

15 Figure 13 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 14.

Figure 14 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 15.

20 Figure 15 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 16.

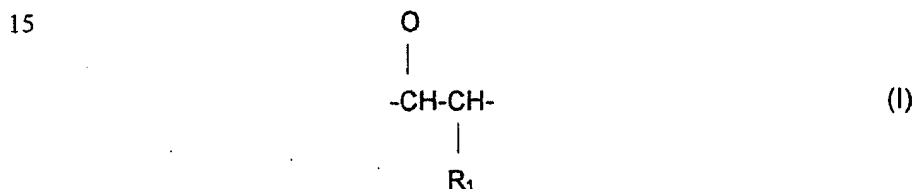
Figure 16 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 17.

Detailed Description of Preferred Embodiments

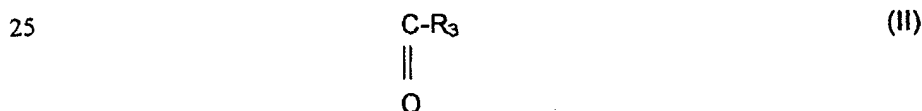
25 The present invention provides a method of influencing the rheology, and particularly reducing the viscosity, of invert (water-in-oil) emulsions and drilling fluids or well service fluids comprising such invert (water-in-oil) emulsions. The method is particularly applicable to fluids for use in wellbores penetrating hydrocarbon bearing subterranean formations. Such drilling fluids and well service fluids typically comprise a continuous oil phase, water
30 dispersed in the oil phase, solids insoluble in the drilling fluid or well service fluid suspended in the fluid, and various additives. As the term is used herein,

an "invert emulsion" or an "oil-in-water emulsion" is understood to mean the liquid portion of a drilling fluid comprising an emulsion (excluding any solids). The term "invert emulsion drilling fluid" means the total sum of what is circulated as a drilling fluid.

- 5 In the method of this invention, certain non-ionic surfactants are added to the invert emulsion or oil based drilling fluid (or well service fluid) to "thin" or reduce the viscosity of the fluid or to enhance the ability of the fluid to maintain its viscosity or to resist increasing viscosity over a broad range of temperatures. The particular non-ionic surfactants are reaction products of ethylene oxide,
 10 propylene oxide and/or butylene oxide with C₁₀₋₂₂ carboxylic acids or C₁₀₋₂₂ carboxylic acid derivatives containing at least one double bond in position 9, 10, 13, or 14 (and preferably one or two double bonds in position 9/10 and/or 13/14) having structural units of the general formula (I)



- 20 where R₁ is a hydrogen atom, or an OH group, or a group OR₂. R₂ is an alkyl group of about 1 to about 18 carbon atoms, or an alkenyl group of about 2 to about 18 carbon atoms, or a group of the formula (II)



- 30 R₃ is a hydrogen atom, or an alkyl group of about 1 to about 21 carbon atoms, or an alkylene group of about 2 to about 21 carbon atoms.

The alkoxylation products may be prepared in accordance with the teaching of DE 39 23 394, which is incorporated herein by reference, by reacting the OH-containing carboxylic acid derivatives, for example, with

ethylene oxide, propylene oxide and/or butylene oxide in the presence of an appropriate catalyst at temperatures between about 110 and about 200°C and pressures between about 10^5 Pa and about 2×10^6 Pa.

Suitable starting materials for OH-containing C_{10-22} carboxylic acids or C_{10-22} carboxylic acid derivatives are unsaturated, naturally occurring and/or synthesizable C_{10-22} carboxylic acids or derivatives thereof containing carboxylic acid radicals having at least one or two double bonds in position 9, 10, 13 and/or 14. Examples of such unsaturated carboxylic acid derivatives are 9-dodecenoic acid, 9-tetradecenoic acid, 9-hexadecenoic acid, 9-octadecenoic acid, 9-octadecenoic acid, 9,12-octadecadienoic acid, 9,12,15-octadecatrienoic acid, 9-icosenoic acid, 13-docosenoic acid, and mixtures containing a large amount (i.e., preferably at least about 60%) of such unsaturated carboxylic acids. As starting materials it is preferable to use carboxylic acids having about 16 to about 22 carbon atoms and at least one or two double bonds in position 9 and/or 13 or carboxylic acid mixtures containing at least a large amount (i.e., preferably at least about 80%) of carboxylic acids having about 16 to about 22 carbon atoms and at least one or two double bonds in position 9 and/or 13.

Further examples of suitable unsaturated carboxylic acid derivatives for use in preparing thinner compounds for use in the invention are unsaturated C_{10-22} carboxylic esters, such as for example, unsaturated C_{10-22} carboxylic acid alkyl esters with monohydric alcohols having about 1 to about 18 carbon atoms. Particularly appropriate are C_{10-22} carboxylic mono-, di- and/or triglycerides containing unsaturated C_{10-22} carboxylic acid radicals having at least one or two double bonds in position 9 and/or 13. Also suitable are esters of C_{10-22} carboxylic acids with other polyols, such as for example ethylene glycol or trimethylolpropane.

Unsaturated C_{10-22} carboxylic acid C_{1-18} alkyl esters are obtainable by esterifying the corresponding unsaturated carboxylic acid or by transesterifying the corresponding mono-, di- and/or triglycerides with C_{1-18} alkyl alcohols, such as, for example, methanol, ethanol, propanol, butanol, isobutanol, 2-ethylhexanol, decanol and/or stearyl alcohol. Examples of such unsaturated

C₁₀₋₂₂ carboxylic acid C₁₋₁₈ alkyl esters are methyl palmitate, methyl oleate, ethyl oleate, isobutyl oleate, 2-ethylhexyl oleate and/or dodecyl oleate and/or C₁₀₋₂₂ carboxylic acid C₁₋₁₈ alkyl ester mixtures containing at least a large fraction (i.e., at least about 60%) of those C₁₀₋₂₂ carboxylic acid C₁₋₁₈ alkyl esters whose carboxylic acid radicals have at least one or two double bonds in position 9 and/or 13, such as, for example, palm oil methyl ester, soya oil methyl ester, colza oil methyl ester and/or tallow fatty acid ethyl ester. Other suitable starting materials for preparing the alkoxylation products for use in the invention are fats and oils of natural origin whose carboxylic acid content is comprised predominantly of unsaturated C₁₀₋₂₂ carboxylic acids having at least one or two double bonds in position 9 and/or 13, such as, for example, olive oil, linseed oil, sunflower oil, soya oil, groundnut oil, cottonseed oil, colza oil, palm oil, lard and tallow.

Unsaturated C₁₀₋₂₂ carboxylic acids and/or C₁₀₋₂₂ carboxylic acid derivatives may be epoxidized to the OH-containing compounds, for example, by reaction with peracetic acid in the presence of acidic catalysts or with performic acid formed *in situ* from formic acid and hydrogen peroxide. The oxirane rings of the epoxidized carboxylic acids and/or carboxylic acid derivatives are subsequently cleaved open to form hydroxyl groups by reaction with hydrogen or protic compounds, such as water, straight-chain and/or branched-chain alkyl and/or alkenyl alcohols having about 1 to about 18 carbon atoms or straight-chain and/or branched-chain, saturated and/or unsaturated C₁₋₁₈ carboxylic acids. Other natural or synthetic compounds comprising epoxide-containing carboxylic acids or carboxylic acid derivatives, such as castor oil or hydrogenated castor oil, may also be used. The cleavage conditions are chosen such that the acid-derivative groups and acid groups present remain intact.

The reaction of epoxidized carboxylic acid derivatives and/or epoxidized carboxylic acids with protic compounds may be carried out, for example, in accordance with the processes described in DE 39 23 394.

The carboxylic acids and/or carboxylic acid derivatives obtained by cleaving the oxirane rings, containing carboxylic acid radicals having at least one OH group in position 9, 10, 13 and/or 14, are subsequently reacted by known industrial processes with ethylene oxide, propylene oxide and/or butylene oxide (preferably with ethylene oxide and/or propylene oxide).

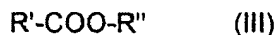
Alkoxylation products obtained by alkoxyating compounds of the formula (I) in which R_1 is a group OR_2 and R_2 is a radical of the formula (II) are preferred. Compounds where the radical R_3 is an alkyl group of about 8 to about 16 carbon atoms, most preferably about 8 to about 10 carbon atoms, are also preferred.

Some non-ionic surfactant compounds that could possibly be used as thinners in accordance with the present invention are also described in WO98/19043 of Henkel Kommandiegesellschaft auf Aktien. That international application teaches use of the compounds in the oil and gas industry as cleaning agents, in contrast to the use of the present invention.

Used as thinners according to the method of the invention, the non-ionic surfactants of the present invention reduce the viscosity or lower the yield point of the drilling fluid to which they are added over a broad range of temperatures.

Example drilling fluids comprising invert (water-in-oil) emulsions of particular use in the method of the invention generally have an oil phase comprising diesel oil, paraffin oil and/or mineral oil, or a synthetic oil. Alternatively, other carrier fluids may be used such as carboxylic esters, alcohols, ethers, internal olefins, alphaolefins (IO and/or AO), and polyalphaolefins (PAO), which may be branched or unbranched but are preferably linear and preferably ecologically acceptable (non-polluting oils). Preferably, the oils or carrier fluids used for the oil phase of the drilling fluid will be comprised of compounds which are flowable and pumpable at temperatures above about 32°F (about 0°C) or as low as about 40°F (about 5°C) as well as at higher temperatures. For example, compounds selected from one or more of the following groups or classes below are believed particularly suitable to comprise the oil phase of drilling fluids used in the present invention:

- (a) most preferably, carboxylic esters of the formula:

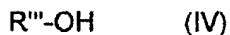


where R' is a saturated or unsaturated, linear or branched, alkyl radical having about 1 to about 23 carbon atoms and R'' is an alkyl radical, branched or unbranched, saturated or unsaturated, having about 1 to about 23 carbon atoms;

- (b) also preferably, linear or branched olefins having about 8 to about 30 carbon atoms;

- (c) water-insoluble symmetric or asymmetric ethers of monohydric alcohols of natural or synthetic origin, said alcohols containing about 1 to about 24 carbon atoms;

- (d) water-insoluble alcohols of the formula:



where R''' is a saturated, unsaturated, linear or branched, alkyl radical having about 8 to about 24 carbon atoms; and

- (e) carbonic diesters.

Such suitable oils are taught further, for example, in: European Patent Applications 0 374 671, 0 374,672, 0 382 070, and 0 386 638 of Cognis; European Laid-Open Specification 0 765 368 of Cognis (linear olefins); European Application 0 472 557 (water insoluble symmetric or asymmetric ethers of monohydric alcohols of natural or synthetic origin containing about 1 to about 24 carbon atoms); European Application 0 532 570 (carbonic diesters). Carboxylic esters of formula (III) above are preferred for the oil phase of drilling fluids used in this invention and particularly preferred are the esters described in European Laid-Open Specification EP 0 374 672 and EP 0 386 636.

In a preferred embodiment of this invention, non-ionic surfactants of the invention are added to drilling fluids comprising invert emulsions having an oil phase comprising esters of formula (III) where the radical R' in formula (III) is

an alkyl radical having about 5 to about 21 carbon atoms (or more preferably about 5 to about 17 carbon atoms or most preferably about 11 to about 17 carbon atoms). Particularly suitable alcohols for making such esters are branched or unbranched alcohols with about 1 to about 8 carbon atoms, for example, methanol, isopropanol, isobutanol, and 2-ethylhexanol. Alcohols having about 12 to about 18 carbon atoms may alternatively be preferred for making other esters suitable for the invention.

For example, additional preferred esters for the oil phase of drilling fluids used in the invention include, without limitation: saturated C12-C14 fatty acid esters and unsaturated C16-C18 fatty acids (with isopropyl-, isobutyl- or 2-ethylhexanol as the alcohol component); 2-ethylhexyl octanoate; acetic acid esters, especially acetates of C8-C18 fatty alcohols; branched carboxylic esters disclosed in WO 99/33932 of Chevron or EP 0 642 561 of Exxon; alpha olefin mixtures disclosed in EP 0 765 368 A1 of Cognis and Halliburton; and blends of these various esters.

The oil phase of the emulsions of the drilling fluids used in the invention is preferably comprised of at least about 50% by volume of one or more preferred compounds (a) – (e) above. More preferably, such preferred compounds comprise about 60% to about 80% by volume of said oil phase, and most preferably, such preferred compounds comprise about 100% of the oil phase.

Water is preferably present in the liquid phase of the emulsions of the drilling fluids used in the invention in amounts preferably not less than about 0.5% by volume (excluding solids in the liquid phase). In a preferred embodiment of this invention, the nonionic surfactant thinners of the present invention are added to drilling fluids (preferably comprising invert emulsions) containing about 15% to about 35% by volume water and more preferably about 20% by volume water and about 80% by volume oil phase.

To compensate for the osmotic gradient between the drilling mud and the formation or connate water, water in drilling fluids used in the present invention typically includes fractions of electrolytes, such as calcium salts

and/or sodium salts. CaCl_2 in particular is frequently used, although other salts from the group of alkali metals and/or alkaline earth metals are also suitable, with potassium acetates and formates being common examples.

Preferred drilling fluids used in this invention have the following
5 rheology: plastic viscosity (PV) preferably in the range of about 10 to about 60 cP, and more preferably in the range of about 15 to about 40 cP, and yield point (YP) preferably in the range of about 5 to about 40 lb/100 ft², and more preferably in the range of about 10 to about 25 lb/100 ft², when measured at about 122°F (about 50°C). At lower temperatures, i.e., at or below about 40°F
10 (about 4°C), the YP should not exceed about 75 lb/100 ft², and should preferably be in the range of about 10 to about 65 lb/100 ft², more preferably about 15 to about 45 lb/100 ft², and most preferably less than about 35 lb/100 ft². A preferred practicable lower limit for YP for drilling fluids used in this invention is about 5 lb/100 ft².

15 Methods for determining these parameters of PV and YP are well known to those skilled in the art. An example reference is "Manual of Drilling Fluids Technology", particularly the chapter on Mud Testing, available from Baroid Drilling Fluids, Inc., in Houston, Texas (USA) and Aberdeen, Scotland, incorporated herein by reference.

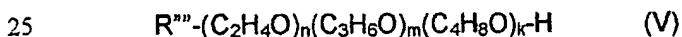
20 The solids content (not including low gravity solids), or amount of weighting agents, in drilling fluids used in this invention is preferably about 0 to about 500 lb/bbl, and most preferably about 150 to about 350 lb/bbl. The mud weight, i.e., the density of the drilling fluids, is preferably in the range of about 8 to about 18 lb/gal. and more preferably about 9 to about 15 lb/gal. Such solids,
25 or weighting agents, which serve to increase density of the drilling fluids, may be any solids known to those skilled in the art as useful for such purpose, but will preferably be inert or environmentally friendly. Barite and barium sulfate are examples of commonly used weighting agents.

Drilling fluids used in this invention may optionally also contain other
30 additives known to those skilled in the art, such as fluid-loss control additives and emulsifiers. Alkali may also be used, preferably lime (calcium hydroxide

or calcium oxide), to bind or react with acidic gases (such as CO₂ and H₂S) encountered during drilling in the formation. Such alkali, or an alkali reserve, is known to prevent hydrolysis by acidic gases of generally acid-labile esters of the drilling fluid. Preferred quantities of free lime in the drilling fluids may range
 5 from about 1 to about 10 lbs/bbl, and more preferably about 1 to about 4 lbs/bbl, although lower ranges such as less than about 2 lbs/bbl are preferred for certain esters that tend to hydrolyze in the presence of alkaline compounds as will be known to those skilled in the art. Other suitable agents as an alternative to lime may also be used to adjust and/or stabilize invert emulsions
 10 of the drilling fluids with respect to acids. An example of such alternative agents is a protonated amine, as described in U.S Patent No. 5,977,031.

Further optional additives that may be present in the drilling fluids used in this invention include electrolytes, such as calcium chloride, organophilic bentonite and organophilic lignite. Glycols and/or glycerol may also be added.
 15 Still further, dispersion aids, corrosion inhibitors and/or defoamers may be used. These and other suitable auxiliaries and additives are used in amounts known to those skilled in the art depending on the conditions of the particular wellbore and subterranean formation.

In an alternative embodiment of the present invention, in addition to the
 20 non-ionic surfactant thinners of the present invention described above, additional thinners may be added advantageously in combination with said non-ionic surfactant thinners. Such particularly advantageous co-thinners are alkoxyated compounds of the general formula (V) :



where R''' is a saturated or unsaturated, linear or branched, alkyl radical having about 8 to about 24 carbon atoms, n is a number ranging from about 1 to about 10, m is a number ranging from about 0 to about 10, and k is a number ranging
 30 from about 0 to about 10. Preferably, R''' has about 8 to about 18 carbon atoms; more preferably, R''' has about 12 to about 18 carbon atoms; and most

preferably, R''' has about 12 to about 14 carbon atoms. Also, most preferably, R''' is saturated and linear.

The compositions or compounds of formula (V) may be prepared by customary techniques of alkoxylation, such as alkoxyating the corresponding
5 fatty alcohols with ethylene oxide and/or propylene oxide or butylene oxide under pressure and in the presence of acidic or alkaline catalysts as is known in the art. Such alkoxylation may take place blockwise, i.e., the fatty alcohol may be reacted first with ethylene oxide, propylene oxide or butylene oxide and subsequently, if desired, with one or more of the other alkylene oxides.
10 Alternatively, such alkoxylation may be conducted randomly, in which any desired mixture of ethylene oxide, propylene oxide and/or butylene oxide is reacted with the fatty alcohol.

In formula (V), the subscripts n and m respectively represent the number of ethylene oxide (EO) and propylene oxide (PO) molecules or groups in one
15 molecule of the alkoxyated fatty alcohol. The subscript k indicates the number of butylene oxide (BO) molecules or groups. The subscripts n , m , and k need not be integers, since they indicate in each case statistical averages of the alkoxylation. Included without limitation are those compounds of the formula (V) whose ethoxy, propoxy, and/or butoxy group distribution is very narrow,
20 such as for example, "narrow range ethoxylates" also called "NREs" by those skilled in the art.

To accomplish the purposes of this invention, the compound of formula (V) must contain at least one ethoxy group and may have up to or about 10 ethoxy groups. Preferably, the compound of formula (V) will also contain at
25 least one propoxy group (C_3H_7O-) or butoxy group (C_4H_9O-). Mixed alkoxides containing all three alkoxide groups—ethylene oxide, propylene oxide, and butylene oxide—are possible for the invention but are not preferred.

Preferably, for use according to this invention, the compound of formula (V) will have a value for m ranging from about 1 to about 10 with k zero or a
30 value for k ranging from about 1 to about 10 with m zero. Most preferably, m will be about 1 to about 10 and k will be zero.

Other preferred compounds for use in the invention having the formula (V) above will have n ranging from about 1 to about 6, m ranging from about 1 to about 6, and k zero. Still other preferred compounds for use in the invention having the formula (V) above will have n ranging from about 2 to about 5, and
5 m being about 3 or about 4 with k zero. It is particularly advantageous to establish the distribution of ethylene oxide and propylene oxide groups in the compounds of formula (V) in an ethylene oxide to propylene oxide ratio of about 1:1 to about 2:1, or even more preferably, about 2:1.5.

Additional preferred compounds for use in the invention having formula
10 (V) above will have alkyl radicals containing about 12 to about 18 carbon atoms, or more preferably about 12 to about 14 carbon atoms, with subscripts n and m each having values of about 4 or about 5.

Both the non-ionic surfactant thinners of the present invention and the thinners of formula (V) may be added to the drilling fluid (or well service fluid)
15 during initial preparation of the fluid or later as the fluid is being used for drilling or well-service purposes in the formation. Alternatively, the non-ionic surfactant thinners may be added first at either of these times and the thinners of formula (V) may be added later. In still another embodiment, the thinners of formula (V) may be added first during either of these times and the non-ionic surfactant
20 thinners of the invention may be added later.

The quantity of thinners added is an effective amount to maintain or effect the desired viscosity of the drilling fluid, preferably or particularly over a broad temperature range. For purposes of this invention, an "effective amount" of non-ionic surfactant thinner is preferably from about 0.5 to about 15 pounds
25 per barrel of drilling fluid or mud. A more preferred amount of surfactant thinner ranges from about 1 to about 5 pounds per barrel of drilling fluid and a most preferred amount is about 1.5 to about 3 pounds thinner per barrel of drilling fluid. When the non-ionic surfactant thinners are used with formula (V) thinners, it is preferred to use the non-ionic surfactant thinners of the present
30 invention and the thinners of formula (V) in proportions of from about 1:1 to about 10:1.

The thinners of the present invention are biodegradable and are of little or no toxicity. They are expected to be capable of meeting increasingly stringent environmental regulations affecting the oil and gas industry worldwide.

Although the invention has primarily been described in the context of a method of using non-ionic surfactants alone and in combination with the compounds of formula (V) as thinners for drilling fluids over a broad temperature range, these non-ionic surfactants alone and in combination with compounds of formula (V) may also be effective as thinners for well service fluids such as spotting fluids or workover fluids over a broad temperature range.

Further description and use of the invention is shown by the following examples:

Examples

To show the effect of the invention, the following experiments were conducted. In each case an invert emulsion drilling mud system of the following general composition was prepared:

Ester	Bbl	0.496
Water	bbl	0.233
Emulsifier	lb	6.0
Organophilic bentonite	lb	1.0
Organophilic lignite	lb	5.0
Alkali reserve (lime)	lb	1.5
CaCl ₂ x 2 H ₂ O	lb	27.2
Barite	lb	314.0
Rev. dust	lb	45.5
Dispersing auxiliary	lb	0.5

Thinner	lb/bbl	3.0
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The oil phase (A) used was a 2-ethylhexyl octanoate as disclosed in EP 0 386 636. The emulsifier used was the product EZ MUL NTE (Baroid Drilling Fluids Inc., Houston, Texas). The oil/water ratio was 70/30 in each case. Measurements were carried out on a system without thinner (C1), and
5 with four non-ionic surfactant thinners E1 to E4 of the invention.

- E1 RS1100™, of Cognis, Germany, see below
- E2 like E1, but reacted with 39 parts of ethylene oxide
- E3 like E1, but reacted with no parts of ethylene oxide
- 10 E4 like E3, but reacted with 25 parts of ethylene oxide
- E5 like E1, but reacted with 50 parts of ethylene oxide

E1 was prepared according to the procedure described in U.S. Patent NO. 5,237,080 to Dante et al., assigned to Henkel Kommandiengesellschaft auf
15 Aktien, by reacting fatty acids (60% C₈, 35% C₁₀, AN = 361.9) with soya oil epoxide and distilling the product to obtain a clear yellow polyol (viscosity = 5550 mPas; 20°C; OHN = 105, SN = 236, AN = 3.1). This reaction product was then admixed with potassium hydroxide in methanol and heated, after which all traces of methanol were removed. The product was then reacted with
20 61 parts of ethylene oxide at a pressure not exceeding 5 bar to yield, after neutralization, a clear yellow liquid (OHN = 54.7). This product may be obtained from Cognis, Germany, under the tradename RS 1100.

The invert drilling fluids or muds were prepared in a conventional manner and subsequently, at 40°F and 120°F, the rheological characteristics of
25 plastic viscosity (PV) and yield point (YP) and the gel strength after 10 seconds and 10 minutes using a Fann SR12 rheometer (from Fann) were determined.

The results of the measurements are given in Table 1:

HALB:017

Table 1

	C1	C1	E1	E1	E2	E2	E3	E3	E4	E4	E5	E5
Temperature °F	40	120	40	120	40	120	40	120	40	120	40	20
PV (cP)	118	40	106	45	111	12	37	110	107	34	100	31
YP lb/100 ft ²	38	14	32	10	26	35	20	53	21	7	15	4
Gels 10"/10'	16/22	6/11	7/8	3/5	13/22	5/8	8/4	20/30	9/14	4/5	6/10	3/5

The data, especially for the yield point (YP), clearly indicate the advantageous thinning effect of the non-ionic surfactant thinners used according to the invention.

Further experiments may be seen in Tables 2 to 17. In these cases, the yield point (YP) of the systems tested was investigated at different temperatures and depicted as a graph. The measurements were carried out using a Fann 35 viscometer (from Fann). The tables also indicate the dial readings at different speeds of rotation per minute (rpm).

In Tables 2 to 17:

10 PETROFREE LV® is 2-ethylhexyl octanoate (Cognis, Germany)
 PETROFREE® is C8-14 fatty acid 2-ethylhexyl ester (Cognis)
 GELTONE II® is organophilic bentonite (Baroid, Houston,
 Texas)
 Thinner E1 is RS 1100™ (Cognis)
15 E1, E2, E3, E4, and E5 are the same as indicated above and as in
 Table 1.

Table 2

Mud system	PETROFREE			
Mud weight, lb/gal	9.5			
Oil/water ratio	70/30			
E1, lb/bbl	0		1	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	75	26	78	23
Yield point, lb/100ft ²	62	31	29	15
10 sec gel, lb/100ft ²	26	16	23	8
10 min gel, lb/100ft ²	27	17	23	10
Fann 35 dial readings				
600 rpm	212	83	185	61
300 rpm	137	57	107	38
200 rpm	110	47	79	30
100 rpm	77	36	49	20
6 rpm	30	18	14	9
3 rpm	26	16	11	7

Table 3

5

Mud system	PETROFREE			
Mud weight, lb/gal	14.0			
Oil/water ratio	75/25			
Contaminant	Excess GELTONE II			
E1	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	180	51	140	36
Yield point, lb/100ft ²	230	152	19	8
10 sec gel, lb/100ft ²	108	64	7	3
10 min gel, lb/100ft ²	110	66	13	4
Fann 35 dial readings				
600 rpm	590	254	299	80
300 rpm	410	203	159	44
200 rpm	336	179	110	30
100 rpm	248	146	62	18
6 rpm	112	79	8	3
3 rpm	100	70	6	2

Table 4

Mud system	PETROFREE			
Mud weight, lb/gal	11.0			
Oil/water ratio	70/30			
Contaminant	Drill solids			
E1, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	11	34	108	35
Yield point, lb/100ft ²	90	47	27	7
10 sec gel, lb/100ft ²	38	21	4	3
10 min gel, lb/100ft ²	44	24	7	5
Fann 35 dial readings				
600 rpm	310	115	243	77
300 rpm	200	81	135	42
200 rpm	157	67	95	30
100 rpm	110	50	52	17
6 rpm	42	23	7	3
3 rpm	38	21	5	2

5 Table 5

Mud system	PETROFREE			
Mud weight, lb/gal	11.0			
Oil/water ratio	70/30			
Contaminant	Excess GELTONE II			
E1, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	132	31	62	18
Yield point, lb/100ft ²	54	53	11	3
10 sec gel, lb/100ft ²	33	23	3	2
10 min gel, lb/100ft ²	38	27	5	3
Fann 35 dial readings				
600 rpm	318	115	135	39
300 rpm	186	84	73	21
200 rpm	139	71	52	14
100 rpm	91	54	29	9
6 rpm	35	25	4	2
3 rpm	32	21	3	1

Table 6

Mud system	PETROFREE LV			
Mud weight, lb/gal	14.0			
Oil/water ratio	70/30			
Contaminant	Drill solids			
E1, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	118	40	106	45
Yield point, lb/100ft ²	38	14	32	10
10 sec gel, lb/100ft ²	16	6	7	3
10 min gel, lb/100ft ²	22	11	8	5
Fann 35 dial readings				
600 rpm	274	94	244	100
300 rpm	156	54	138	55
200 rpm	114	40	98	39
100 rpm	70	25	55	22
6 rpm	17	6	8	4
3 rpm	14	5	5	3

5

Table 7

Mud system	PETROFREE LV			
Mud weight, lb/gal	14.0			
Oil/water ratio	70/30			
Contaminant	Drill solids			
E5, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	110	37	100	31
Yield point, lb/100ft ²	53	20	15	4
10 sec gel, lb/100ft ²	20	8	6	3
10 min gel, lb/100ft ²	30	14	10	5
Fann 35 dial readings				
600 rpm	273	94	215	66
300 rpm	163	57	115	35
200 rpm	124	42	80	25
100 rpm	80	27	44	15
6 rpm	23	8	7	3
3 rpm	19	7	5	2

Table 8

Mud system	PETROFREE	
Mud weight, lb/gal	9.5	
Oil/water ratio	70/30	
E5, lb/bbl	0	3
Temperature, °F	120	120
Plastic viscosity, cP	22	21
Yield point, lb/100ft ²	39	16
10 sec gel, lb/100ft ²	16	8
10 min gel, lb/100ft ²	17	10
Fann 35 dial readings		
600 rpm	83	58
300 rpm	61	37
200 rpm	52	28
100 rpm	40	20
6 rpm	19	8
3 rpm	17	7

5 Table 9

Mud system	PETROFREE LV			
Mud weight, lb/gal	9.5			
Oil/water ratio	70/30			
Contaminant	Drill solids			
E5, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	65	20	52	20
Yield point, lb/100ft ²	31	33	27	17
10 sec gel, lb/100ft ²	29	17	17	10
10 min gel, lb/100ft ²	32	22	26	15
Fann 35 dial readings				
600 rpm	151	73	131	57
300 rpm	96	53	79	37
200 rpm	78	44	66	30
100 rpm	57	34	29	20
6 rpm	29	18	14	9
3 rpm	27	16	12	8

Table 10

Mud system	PETROFREE			
Mud weight, lb/gal	14.0			
Oil/water ratio	75/25			
Contaminant	Excess GELTONE II			
E5, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	180	51	175	47
Yield point, lb/100ft ²	230	152	34	10
10 sec gel, lb/100ft ²	108	64	10	3
10 min gel, lb/100ft ²	110	66	14	5
Fann 35 dial readings				
600 rpm	590	254	384	104
300 rpm	410	203	209	57
200 rpm	336	179	148	40
100 rpm	248	146	82	23
6 rpm	112	79	12	3
3 rpm	100	70	9	2

5 Table 11

Mud system	PETROFREE			
Mud weight, lb/gal	11.0			
Oil/water ratio	70/30			
Contaminant	Drill solids			
E5, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	110	34	106	30
Yield point, lb/100ft ²	90	47	20	9
10 sec gel, lb/100ft ²	38	21	8	5
10 min gel, lb/100ft ²	44	24	11	9
Fann 35 dial readings				
600 rpm	310	115	232	69
300 rpm	200	81	126	39
200 rpm	157	67	88	28
100 rpm	110	50	49	17
6 rpm	42	23	9	5
3 rpm	38	21	7	4

Table 12

Mud system	PETROFREE			
Mud weight, lb/gal	11.0			
Oil/water ratio	70/30			
Contaminant	Excess GELTONE II			
E5, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	132	31	90	23
Yield point, lb/100ft ²	54	53	20	9
10 sec gel, lb/100ft ²	33	23	6	2
10 min gel, lb/100ft ²	38	27	9	3
Fann 35 dial readings				
600 rpm	318	115	200	55
300 rpm	186	84	110	32
200 rpm	139	71	77	22
100 rpm	91	54	42	13
6 rpm	35	25	6	2
3 rpm	32	21	4	1

Table 13

Mud system	PETROFREE LV			
Mud weight, lb/gal	14.0			
Oil/water ratio	70/30			
Contaminant	Drill Solids			
E1, lb/bbl	0		1	
E2, lb/bbl	0		2	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	118	40	105	33
Yield point, lb/100ft ²	38	14	15	6
10 sec gel, lb/100ft ²	16	6	7	3
10 min gel, lb/100ft ²	22	11	12	6
Fann 35 dial readings				
600 rpm	274	94	225	72
300 rpm	156	54	120	39
200 rpm	114	40	83	28
100 rpm	70	25	45	16
6 rpm	17	6	7	3
3 rpm	14	5	5	2

Table 14

Mud system	PETROFREE LV					
Mud weight, lb/gal	14.0					
Oil/water ratio	70/30					
Contaminant	Drill solids (5%)					
E2, lb/bbl	0	3	5			
Temperature, °F	40	120	40	120	40	120
Plastic viscosity, cP	118	40	111	35	114	37
Yield point, lb/100ft ²	38	14	26	7	17	2
10 sec gel, lb/100ft ²	16	6	13	5	6	2
10 min gel, lb/100ft ²	22	11	22	8	9	4
Fann 35 dial readings						
600 rpm	274	94	248	77	245	76
300 rpm	156	54	137	42	131	39
200 rpm	114	40	98	30	91	27
100 rpm	70	25	57	18	50	16
6 rpm	17	6	12	4	6	2
3 rpm	14	5	10	3	4	1

Table 15

Mud system	PETROFREE LV					
Mud weight, lb/gal	14.0					
Oil/water ratio	70/30					
Contaminant	Drill solids (10%)					
E2, lb/bbl	0	5	7			
Temperature, °F	40	120	40	120	40	120
Plastic viscosity, cP	176	59	152	48	150	47
Yield point, lb/100ft ²	48	19	14	6	20	4
10 sec gel, lb/100ft ²	16	9	8	6	8	3
10 min gel, lb/100ft ²	28	17	13	8	10	4
Fann 35 dial readings						
600 rpm	400	137	318	104	320	98
300 rpm	224	78	166	56	170	51
200 rpm	170	57	115	40	118	36
100 rpm	100	34	62	23	64	20
6 rpm	18	8	8	4	8	3
3 rpm	14	7	7	3	6	2

Table 16

Mud system	PETROFREE LV			
Mud weight, lb/gal	14.0			
Oil/water ratio	70/30			
Contaminant	Drill Solids			
E3, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	118	40	115	36
Yield point, lb/100ft ²	38	14	35	14
10 sec gel, lb/100ft ²	16	6	25	6
10 min gel, lb/100ft ²	22	11	30	9
Fann 35 dial readings				
600 rpm	274	94	265	86
300 rpm	156	54	150	50
200 rpm	114	40	110	37
100 rpm	70	25	65	23
6 rpm	17	6	17	5
3 rpm	14	5	13	4

Table 17

Mud system	PETROFREE LV			
Mud weight, lb/gal	14.0			
Oil/water ratio	70/30			
Contaminant	Drill Solids			
E3, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	118	40	115	36
Yield point, lb/100ft ²	38	14	35	14
10 sec gel, lb/100ft ²	16	6	25	6
10 min gel, lb/100ft ²	22	11	30	9
Fann 35 dial readings				
600 rpm	274	94	265	86
300 rpm	156	54	150	50
200 rpm	114	40	110	37
100 rpm	70	25	65	23
6 rpm	17	6	17	5
3 rpm	14	5	13	4

The foregoing description of the invention is intended to be a description of preferred embodiments. Various changes in the details of the described
5 compositions and method can be made without departing from the intended scope of this invention as defined by the appended claims.

We claim:

1. A method of influencing the rheology of a drilling fluid or well service fluid comprising an invert emulsion, said method comprising adding to said fluid at least one non-ionic surfactant, said surfactant being the reaction product of at least one oxide, selected from the group comprising ethylene oxide, propylene oxide and butylene oxide, with C₁₀₋₂₂ carboxylic acids or C₁₀₋₂₂ carboxylic acid derivatives containing at least one double bond in position 9, 10, 13, or 14 having structural units of the general formula (I)



where R₁ is a hydrogen atom, or an OH group, or a group OR₂, and where R₂ is an alkyl group of about 1 to about 18 carbon atoms, or an alkenyl group of about 2 to about 18 carbon atoms, or a group of the formula (II):



and where R₃ is a hydrogen atom, or an alkyl group of about 1 to about 21 carbon atoms, or an alkylene group of about 2 to about 21 carbon atoms.

2. The method of claim 1 wherein said non-ionic surfactant comprises alkylation products obtained by reacting C₁₂₋₂₂ carboxylic mono-, di- or triglycerides containing structural units of the formula (I) in at least one position 9, 10, 13, or 14 with at least one oxide of the group comprising ethylene oxide, propylene oxide, and butylene oxide.

3. The method of claim 1 wherein said drilling fluid or well service fluid comprises a continuous oil phase that is flowable and pumpable at temperatures
5 at least as low as about 40 degrees Fahrenheit.

4. The method of claim 1 wherein said drilling fluid or well service fluid comprises a continuous oil phase that is flowable and pumpable at temperatures
10 above about 32 degrees Fahrenheit.

5. The method of claim 3 wherein said oil phase comprises compounds or compositions selected from the group comprising:

(a) carboxylic esters of the formula:

15
$$R'-COO-R''$$

where R' is a saturated or unsaturated, linear or branched, alkyl radical having about 1 to about 23 carbon atoms and R'' is an alkyl radical, branched or unbranched, saturated or unsaturated, having about 1 to about 23 carbon atoms;

20 (b) linear or branched olefins having about 8 to about 30 carbon atoms;

(c) water-insoluble symmetric or asymmetric ethers of monohydric alcohols of natural or synthetic origin, said alcohols containing about 1 to about 24 carbon atoms;

(d) water-insoluble alcohols of the formula:

25
$$R'''-OH$$

where R''' is a saturated, unsaturated, linear or branched alkyl radical having about 8 to about 24 carbon atoms; and

(e) carbonic diesters.

30 6. The method of claim 5 wherein said oil phase comprises esters wherein the radical R' is an alkyl radical having about 5 to about 21 carbon atoms.

7. The method of claim 1 wherein said surfactant is added to said drilling fluid or well service fluid in an amount sufficient to effect a reduction in the viscosity of said emulsion.

5 8. The method of claim 1 wherein said surfactant is added to said drilling fluid or well service fluid in an amount sufficient to maintain the flowability and pumpability of said emulsion.

9. The method of claim 1 wherein said surfactant is added to said drilling
10 fluid or well service fluid in quantities ranging from about 0.5 pounds to about 15.0 pounds of said compound per barrel of said emulsion.

10. The method of claim 1 further comprising adding to said drilling fluid or well service fluid a co-thinner compound having the formula:

15



where R is a saturated or unsaturated, linear or branched alkyl radical having about 8 to about 24 carbon atoms, n is a number ranging from about 1 to about
20 10, m is a number ranging from about 0 to about 10, and k is a number ranging from about 0 to about 10.

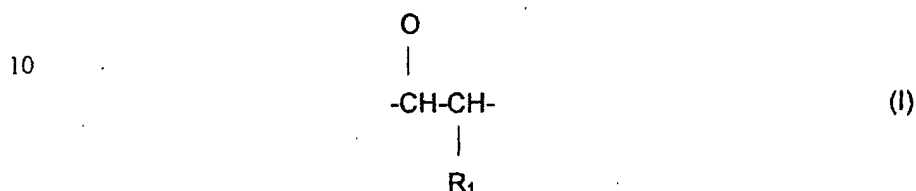
11. The method of claim 10 wherein in said formula for said co-thinner compound, k is zero and m is a number ranging from about 1 to about 10, or m is
25 zero and k is a number ranging from about 1 to about 10.

12. The method of claim 10 wherein in said formula for said co-thinner compound, n is a number ranging from about 1 to about 6, m is a number ranging from about 1 to about 6, and k is zero.

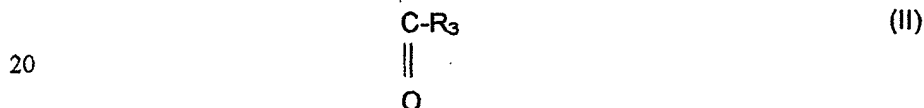
30

13. The method of claim 10 wherein said surfactant and said co-thinner compound are added in proportions ranging from about 1:1 to about 10:1.

14. A drilling fluid or well service fluid comprising a continuous oil phase, water dispersed in said oil phase, solids insoluble in said oil phase, and at least one non-ionic surfactant, said surfactant being the reaction product of ethylene oxide, propylene oxide and/or butylene oxide with C₁₀₋₂₂ carboxylic acids or C₁₀₋₂₂ carboxylic acid derivatives containing at least one double bond in position 9, 10, 13, or 14 having structural units of the general formula (I)



- 15 where R₁ is a hydrogen atom, or an OH group, or a group OR₂, and where R₂ is an alkyl group of about 1 to about 18 carbon atoms, or an alkenyl group of about 2 to about 18 carbon atoms, or a group of the formula (II):



- where R₃ is a hydrogen atom, or an alkyl group of about 1 to about 21 carbon atoms, or an alkylene group of about 2 to about 21 carbon atoms.

15. The drilling fluid or well service fluid of claim 14 wherein said surfactant is added in sufficient amounts to reduce the viscosity of said fluid.

16. The drilling fluid or well service fluid of claim 14 wherein said surfactant is added to said fluid in quantities ranging from about 0.5 pounds to about 15.0 pounds of said surfactant per barrel of said fluid.

17. The drilling fluid or well service fluid of claim 14 having a yield point of not more than about 75 lbs/100 ft² at about 40°F.

18. The drilling fluid or well service fluid of claim 14 further comprising a compound having the formula:



5

where R''' is a saturated or unsaturated, linear or branched alkyl radical having about 8 to about 24 carbon atoms, n is a number ranging from about 1 to about 10, m is a number ranging from about 0 to about 10, and k is a number ranging from about 0 to about 10.

10

19. The drilling fluid or well service fluid of claim 18 wherein said surfactant and said compound are in proportions ranging from about 1:1 to about 10:1.

20. The method of claim 1 wherein said surfactant is added to said drilling fluid or well service fluid during preparation of said fluid or after such fluid has begun service in the wellbore.

21. The method of claim 10 wherein said co-thinner compound is added to said fluid during preparation of said fluid or after said fluid has begun service in the wellbore.

20

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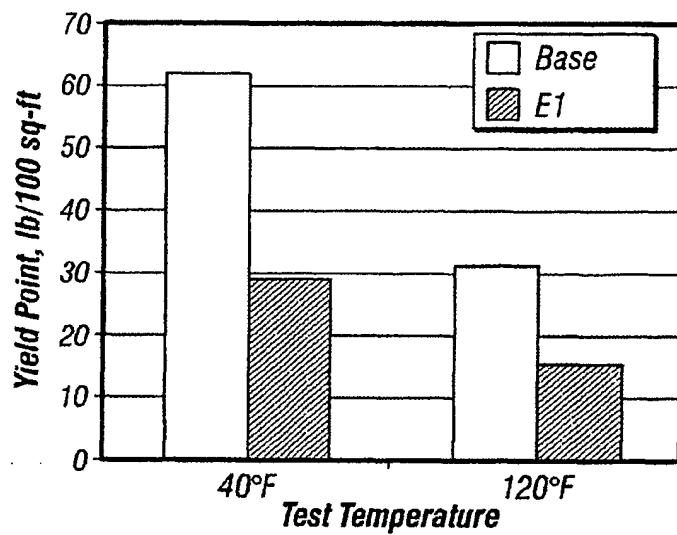


FIG. 1

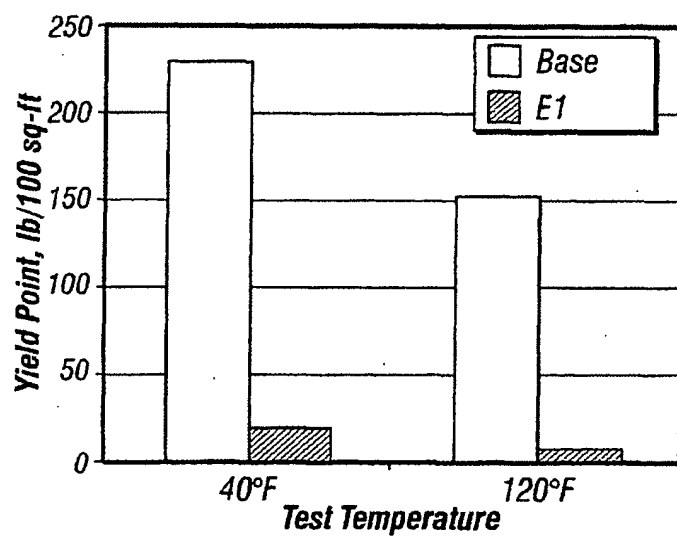


FIG. 2

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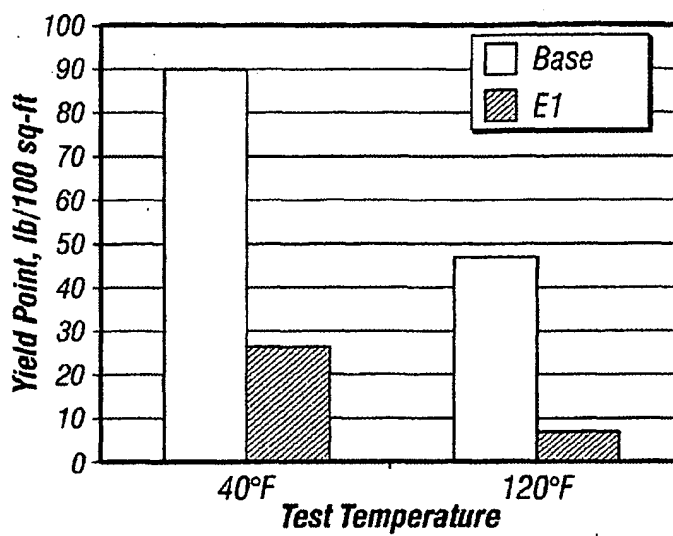


FIG. 3

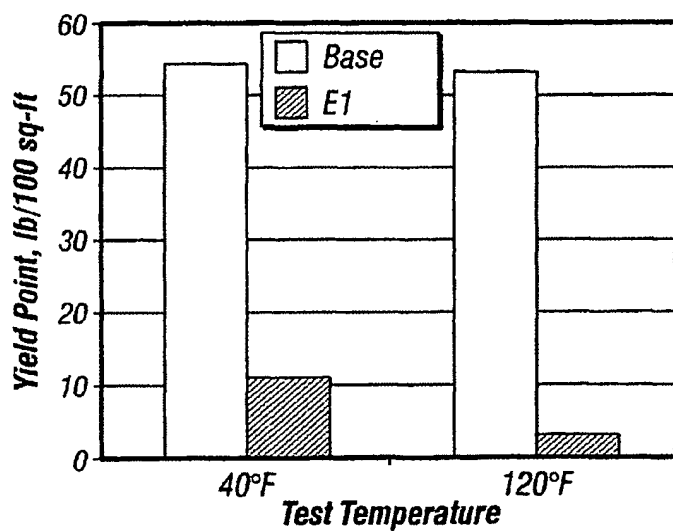


FIG. 4

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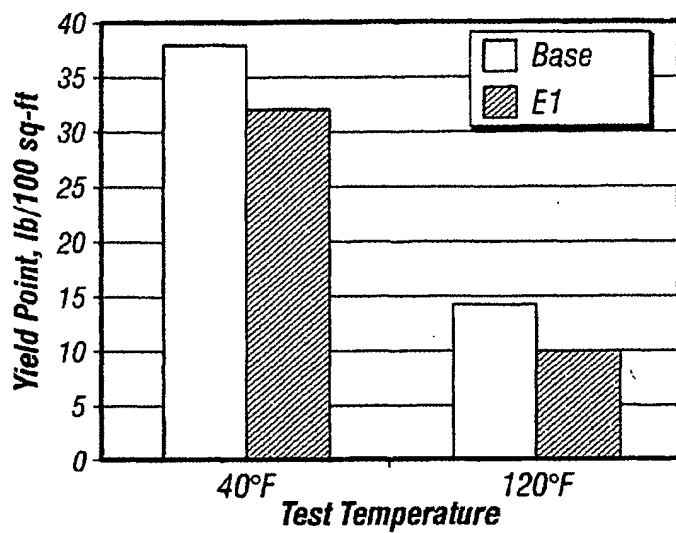


FIG. 5

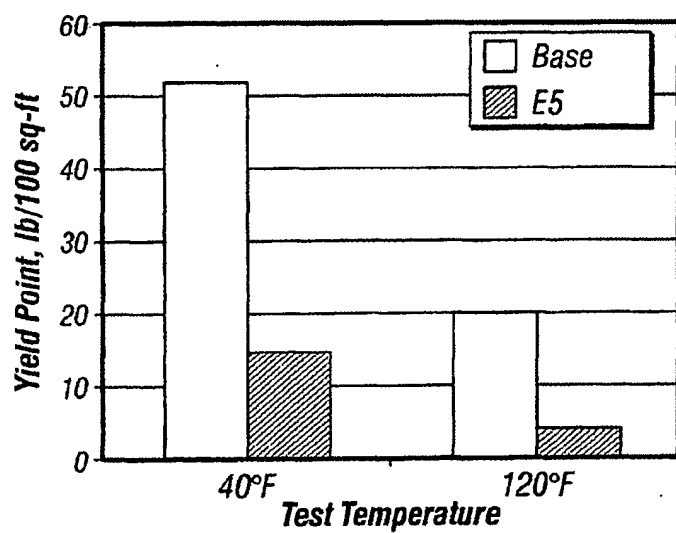


FIG. 6

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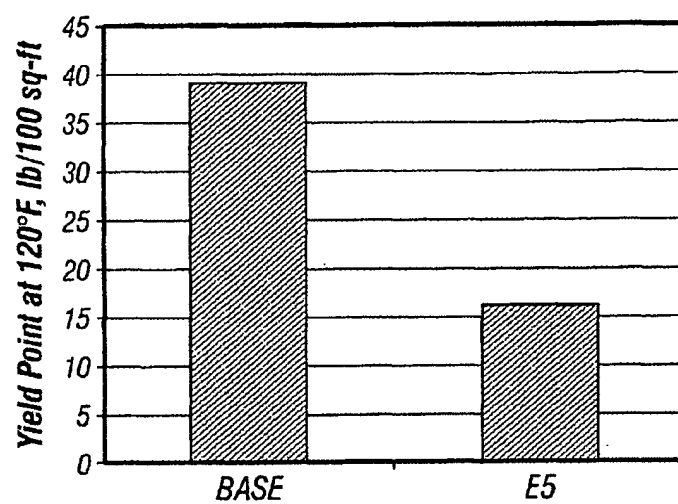


FIG. 7

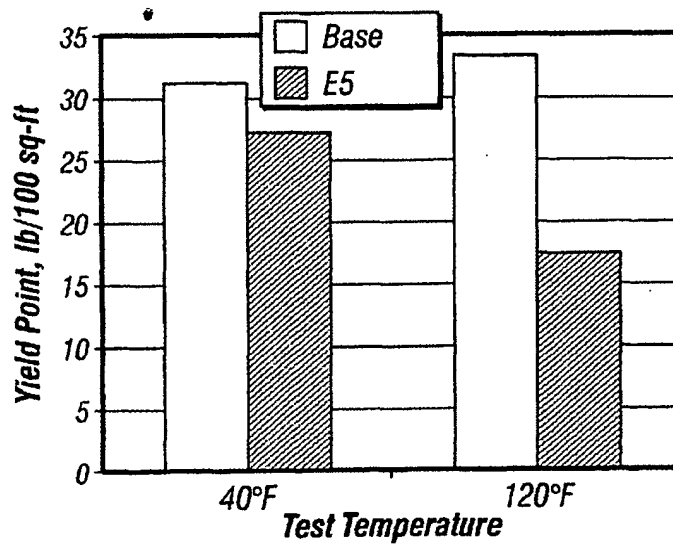


FIG. 8

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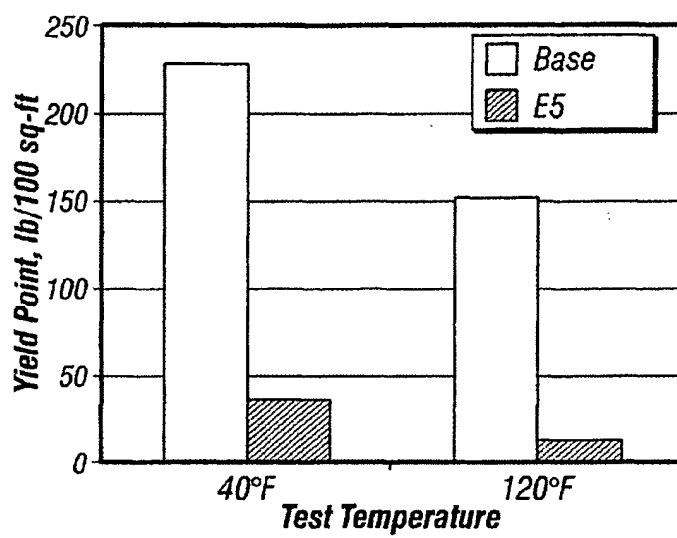


FIG. 9

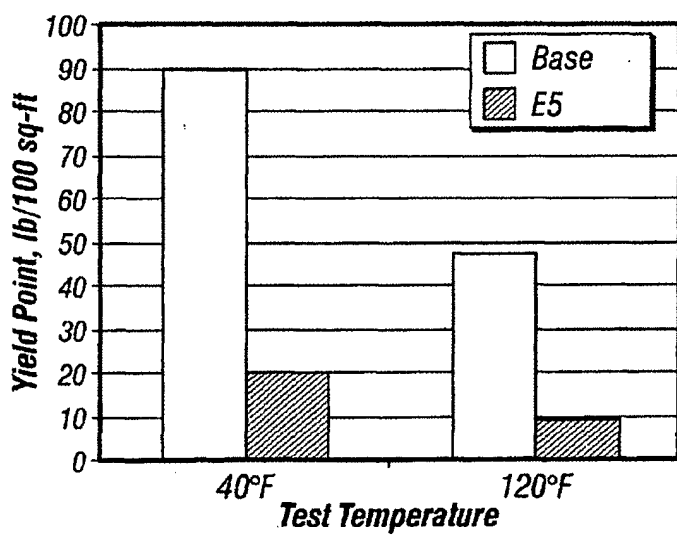


FIG. 10

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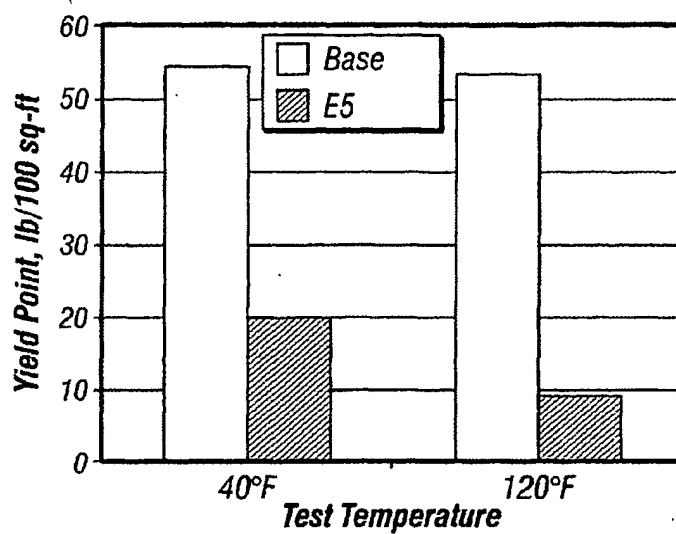


FIG. 11

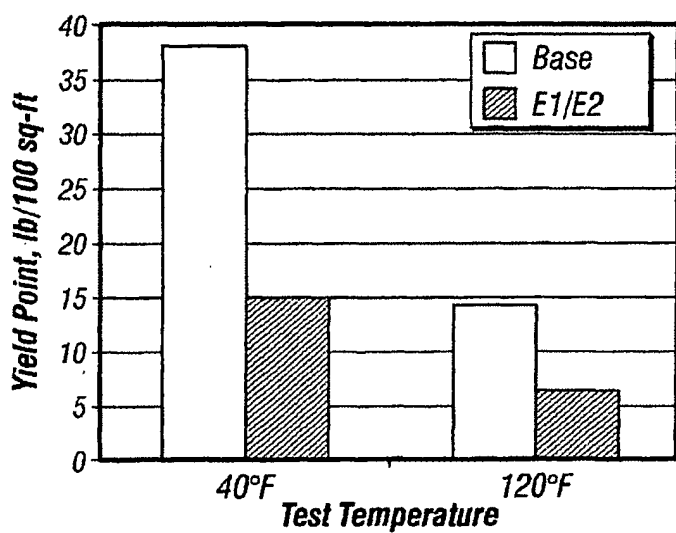


FIG. 12

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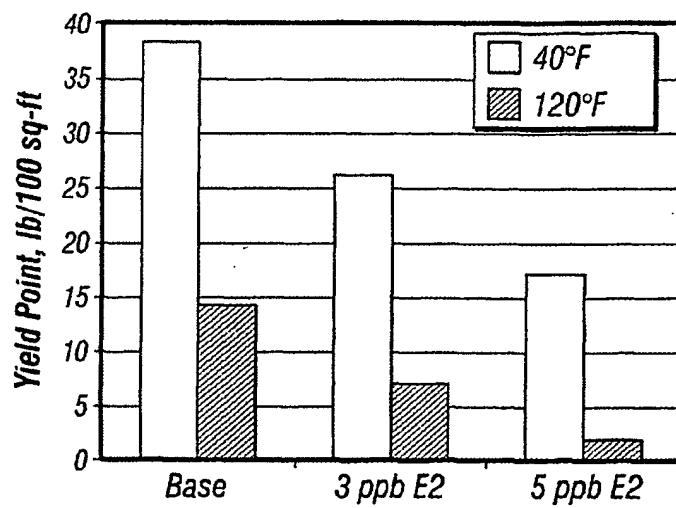


FIG. 13

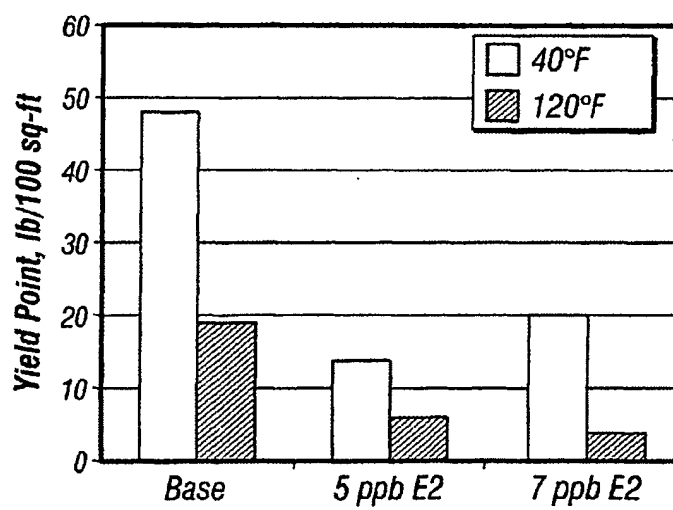


FIG. 14

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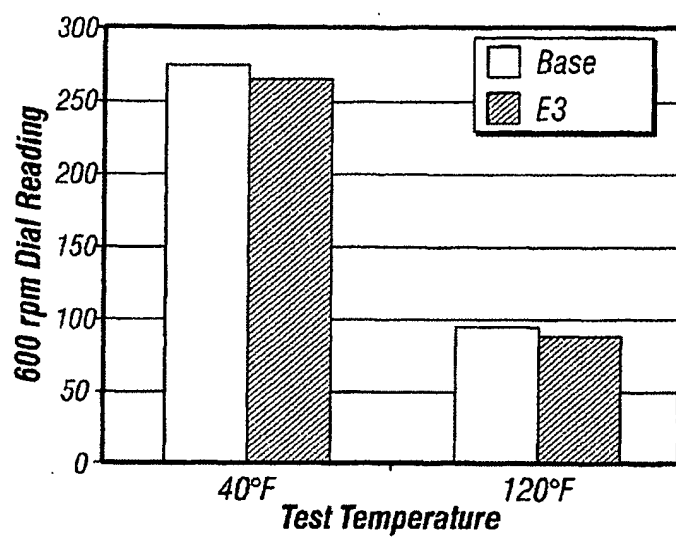


FIG. 15

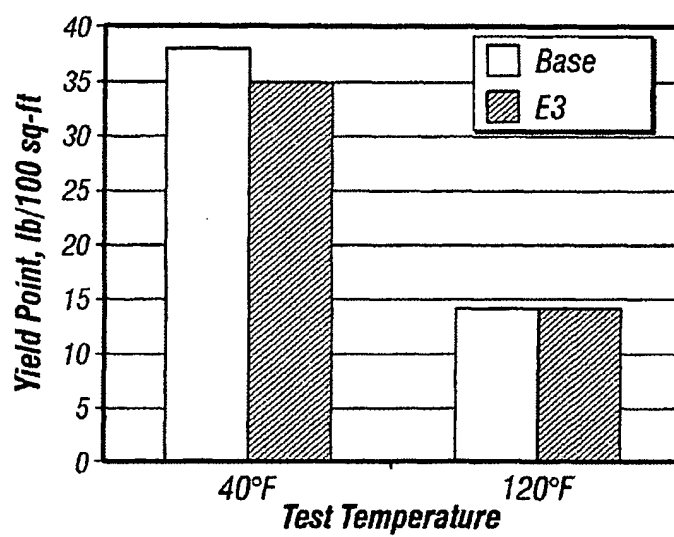


FIG. 16

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/35610A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09K7/06 B01F17/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09K B01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Date of the actual completion of the international search

8 August 2001

Date of mailing of the international search report

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